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Modelling the In Situ Infrared Reflection-Absorption Spectra of the Diffuse Layer

by

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Prepared for Presentation

at

The Electrochemical Society Meeting  
Los Angeles, CA, May 1989

May 1, 1989

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# Modelling the *In Situ* Infrared Reflection-Absorption Spectra of the Diffuse Double Layer.

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The sensitivity of *in situ* IRRAS techniques<sup>1</sup> such as EMIRS and SNIFTIRS to molecular structure at the electrode / electrolyte interface arises from the coupling of two physical phenomena: the local increase in the electric field strength for parallel polarized light reflect at the surface of the electrode<sup>2</sup> and the potential drop across the double layer. In the EMIRS or SNIFTIRS experiment there is enhanced sensitivity to species present within a few wavelengths of the IR radiation from the electrode surface and only to those species which change due to the applied electrochemical potential. As the diffuse layer is typically 10 - 100 Å for these experiments<sup>3</sup> and as the large electromagnetic field at the metal surface decays over much longer distances<sup>4</sup>, 2 - 20 μm, the resultant *in situ* spectra will be a function of the product of these two effects integrated over the complete diffuse layer. Thus with such techniques the diffuse layer is probed to almost the same extent as is the electrode surface.

This paper presents a method for calculating the *in situ* infrared reflection-absorption spectra for species present in the diffuse layer based on a stratified media model of the electrode / electrolyte interface, Gouy-Chapman-Stern theory and the attenuated total reflection IR spectra of the electrolyte solutions.

In order to calculate reflection-absorption spectra it is necessary to construct an optical model of the interface. Figure 1 is a schematic drawing showing an N layer system consisting of a non-absorbing semi-infinite initial phase, N-2 planar finite strata and an absorbing semi-infinite final phase. This approach assumes that the media are isotropic, homogeneous, linear and that the dielectric constant is independent of position within an individual layer.<sup>4,5</sup> Calculations of optical parameters for the *in situ* experiment, based on similar models, have been reported.<sup>6,7</sup>

In this treatment, the matrix formalism developed by Hansen<sup>5</sup> for the N layer system will be apply to a stratified medium where the 3rd through N-2 components represent the diffuse layer as is shown in Figure 1. Each of these N-4 strata will have a dielectric constant and characteristic thickness associated with it, obtained from bulk solution and solvent values and GSC theory. The real and the imaginary components of the dielectric constants are calculated using ATR measurements of the bulk components and the appropriate Fresnel equations.<sup>8,9</sup>

Modelled and measured spectra for gold electrodes, using alkali perchlorate salts in dimethylformamide and acetonitrile solutions will be presented.

## Acknowledgements

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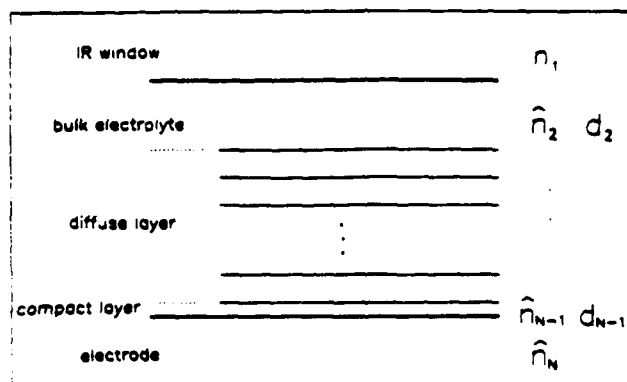


Figure 1. Multiple layer optical model of the electrode / electrolyte interface.